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Robust Microstructures Using UV Photopatternable Semiconductor Nanocrystals

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ABSTRACT

We report an approach to produce predefined patterns of quantum dots and multipod nanocrystals using optical lithography for direct writing of films for optoelectronic and electronic devices. To obtain photopatternability, the nanostructures (for example, CdSe, CdTe, and PbSe nanocrystals) were functionalized by incorporation of the functional ligand *t*-butoxycarbonyl (*t*-BOC) which has an acid-labile moiety. This change in the surface chemistry results in the ability to photopattern the semiconductor nanocrystals where desired for a number of optoelectronic device geometries. We demonstrate that the ultimate resolution (line width and spacing) of this technique is below 5 μm (the limit of our optical apparatus used for writing).

Semiconductor nanocrystals (NCs, also known as quantum dots, QDs) have attracted much attention due to their tunable optical and electrical properties and applications for optoelectronic devices such as light-emitting diodes,[1,2] photodetectors,[3−5] field-effect transistors,[6] photovoltaic cells,[7,8] and photorefractives.[9] QDs are typically synthesized in the form of nanocrystals covered with ligands whose length and chemical constitution are known to play an important role in the charge transport between the NCs.[6,8] The as-synthesized ligands are often bulky and electrically insulating; thus, replacing them with a shorter functional group would be beneficial for electrical applications. In enhanced ligand exchange, several chemical and thermal treatment techniques have been developed to improve the electronic properties of QDs.[6−8,10] An alternative to these approaches might be a technique where light is used to initiate ligand replacement. An additional benefit of this technique is that it might also provide the possibility of photopatterning for direct-write device fabrication. To address this issue, we have developed novel photopatternable NCs that exhibit good solubility in common solvents to enable solution-based processing. There have been several recent papers that have demonstrated the capability to fix nanocrystals at desirable locations. For example, Kim's group has recently demonstrated the ability to create photopatterned quantum nanocrystal films for light-emitting diodes by cross-linking the unsaturated double bonds between ligands such as oleic acid under UV illumination;[11] however, this approach results in bulky and electrically insulated ligands around the semiconductor nanocrystal. In addition, a few of these studies have reported an alternative method to produce photopatterned quantum nanocrystal devices by using a photopatterned polymer template.[12−14] In this paper, we demonstrate a method to produce photopatterned nanocrystal structures with short interconnecting ligands that can be electrically conductive. Moreover, we demonstrate that this technique can provide dual-tone (positive or negative) images for fabrication. As a consequence of proper modification to introduce photopatternability, the new NCs can be used in low-cost fabrication processes such as microlithography in solid-state films using the concept of chemical amplification.[15,16] The use of the NCs instead of organic photoresists may bring advantages to lithography due to the NCs high photostability against light sources such as deep UV.[11,17] Moreover, the photopatterning process, using the chemical amplification reaction, leads to a shortening of the length of the ligands and can thus result in improved electronic properties. In this letter, we report synthesis of photopatternable NCs, their optical characterization, demonstration of robust microstructures by microlithography using these NCs, and the opto-

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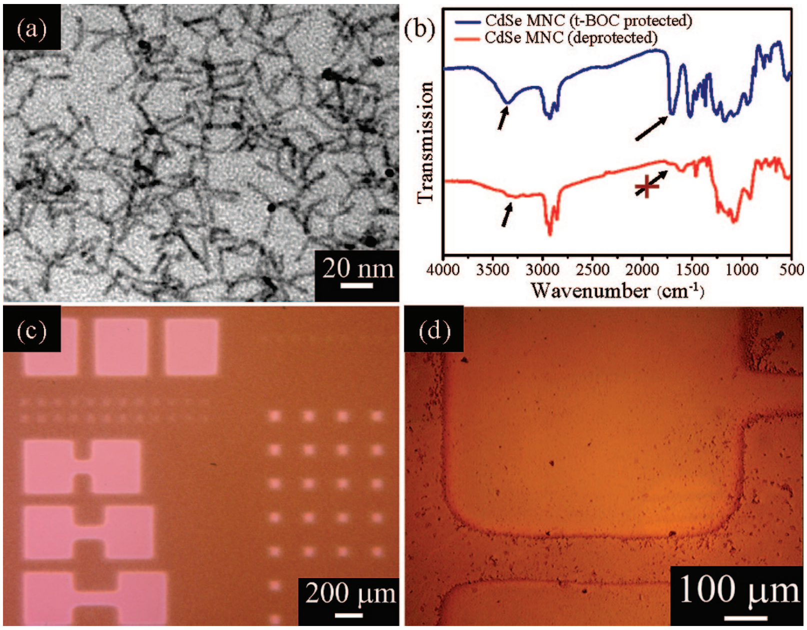
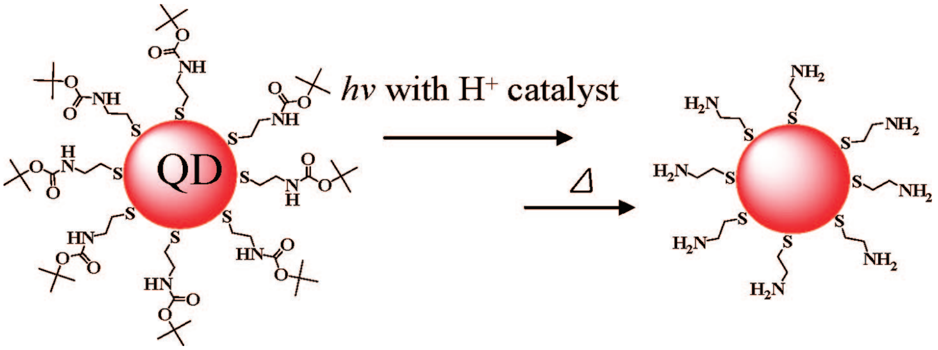


Figure 1. (a) TEM image of CdSe multipod nanocrystals and (b) the corresponding IR spectra of the CdSe MNC, before (blue line) and after (red line) deprotection of *t*-BOC group. Optical microscopy images display the developer solvent-induced dual-tone (negative (c)/positive (d)) imaging using the *t*-BOC protected CdSe multipod NCs.

Scheme 1. Scheme of the Chemical Amplification Reaction



electronic properties of the resulting photopatterned structures.

To demonstrate photopatternability of NCs, we modified CdSe multipod nanocrystals (MNCs) by incorporation of the functional ligand *t*-butoxycarbonyl (*t*-BOC) which has an acid-labile moiety. This modification enables shortening of the ligands and a change in solubility of the QDs by illumination with UV light in the presence of a photoacid-generating compound (PAG). Specifically, CdSe multipod NCs were prepared by using a procedure established in the literature.[18] The typical resident trioctylphosphine oxide, or other in situ generated ligands, were then replaced with the new exchange ligand: *tert*-butyl *N*-(2-mercaptoethyl)carbamate. Subsequently, the obtained *t*-BOC protected CdSe MNCs were examined by optical and transmission electron microscopy (TEM) as shown in Figure 1a.

As shown in Scheme 1, the QD surface is covered with ligands and fully protected with *t*-BOC. It is possible to selectively modify the surface of the NCs, in specific spatial regions, by reaction with the photochemically generated acid under UV irradiation. In this process, the hydrophobic ligands are then converted to hydrophilic ligands. This change enables the developer solvent-induced dual-tone (positive/negative) imaging. To photopattern the films, a nanocrystal solution (30 mg of *t*-BOC protected CdSe multipod NCs and 5 wt % of di-*tert*-butylphenyliodonium perfluorobutanesulfonate as a PAG in 1 mL of chloroform) was spin-casted onto a glass plate. The spin-casted film was exposed to UV light through an optical mask for 10 min and, simultaneously, heated for 90 s at 100 °C. Finally, the exposed films were developed by using two different developers: (i) a hexane based solvent for negative patterns and (ii) an acetone-based solvent for positive patterns. Indeed, the obtained dual-tone images indicate that the hydrophilic affinity of the NCs has increased significantly in the UV exposed regions compared with unexposed regions. In other words, it is the polarity change of the NC surface that is a key factor in providing the image (positive or negative) that is obtained by washing the surface using common solvents. Figure 1 shows examples of photopatterned images obtained using the CdSe multipod NCs lithography as described above. It is evident from this demonstration that the technology offers the possibility of readily creating desired images using standard photolithography techniques.

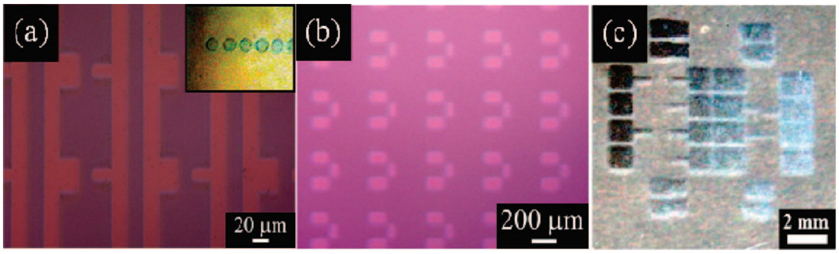


Figure 2. Photopatterned negative images of the CdTe QD (a), CdSe QD (b), and PbSe QD by exposure of QDs and to UV light through a chrome/quartz mask in the presence of the photogenerated acid. (a) Inset displays a 5 μm circle patterned with CdTe QDs.

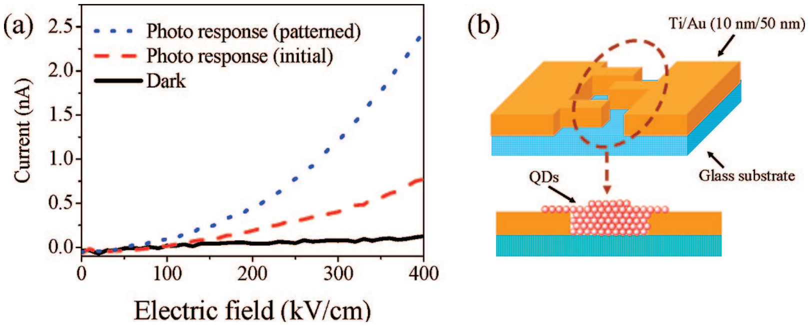


Figure 3. Current−voltage curves (a) in the dark or with white light (100 mW/cm^2) illumination for a film of *t*-BOC protected and deprotected CdTe nanocrystals (measured at the voltage scan rate of 1 V/s). The channel length is 4 μm. MSM device structure (b) for photoconductivity measurement.

To determine the structural conversion of the ligand on the CdSe MNCs solid-state film by deprotection of *t*-BOC, IR spectroscopy was utilized to confirm the chemical structure change. Figure 1b displays representative IR spectra, before and after deprotection. Significant changes are clearly observed between the spectrum of the *t*-BOC protected NCs and the spectrum of the deprotected NCs. Specifically, the strong carbonyl stretching peak at 1702 cm^{-1} disappears after deprotection of the *t*-BOC moiety. Simultaneously, the characteristic absorption peak at 3350 cm^{-1}, attributed to the −NH vibrations, splits into two peaks in the deprotected NCs, suggesting that the secondary amine group changes to a primary amine group through the chemical amplification reaction.

This photopatternability can be introduced into many other types of NCs by the same principle of ligand exchange. We chose quantum dots of PbSe, CdTe, and CdSe as targets for demonstrating the viability and robustness of this approach. Specifically, additional photopatternable quantum dot NCs were synthesized,[6,19,20] the ligands were replaced, and microlithography was demonstrated using the same method as described for the photopatternable CdSe MNCs. Figure 2 shows examples of the resulting patterns after microlithography and demonstrates that patterns with features as small as 5 μm can be readily defined by this process. It is evident that the photopatternable system provides the same controllability in different types of NCs and suggest that this method is robust and should be reproducible for other types of quantum dot nanocrystals (provided that the initial ligand can be replaced with *t*-BOC).

Therefore, it is possible to photopattern these structures using either positive (*t*-BOC protected) or negative (*t*-BOC deprotected) images. The choice of methodology would need to be chosen on the basis of ultimate application of the resulting photopatterned structures. Thus, in addition to the photopatterning of thin films of the NCs, we report preliminary experiments to examine the optoelectronic properties of the two resulting films. Specifically, the photoconductivity of a CdTe nanocrystal based metal semiconductor metal (MSM) detector structure was studied as a function of the protection of the nanocrystals (Figure 3b). In this device, the *t*-BOC protected NC solutions were drop-casted on the device structure shown in Figure 3b. The resulting dark and photocurrent properties of this device were measured. Subsequently, to obtain *t*-BOC deprotected NC devices, the films were exposed under UV and annealed at 100 °C for 2 min.

The resulting current−voltage (*I*−*V*) curves of the CdTe QDs are shown in Figure 3. For a given device system, the photoconductivity increases dramatically when the *t*-BOC groups are removed from the initial CdTe QDs film. The enhancement in photocurrent, compared to a *t*-BOC protected CdTe layer, is by more than 1 order of magnitude. For all the measured devices, it is worth noting that the dark current is always very low, below 0.1 nA, due to the overall insulating nature of the thin film device. It is clear that the length of ligands, fully covering the NC surface, plays a key role for the intercharge transfer between NCs as mentioned above. Thus, even though the photopatternable nanocrystals provide dual-tone imaging, negative images (*t*-BOC deprotected NCs) would be much more applicable for optoelectronic device where efficient charge transport is essential.

Finally, the mobility of the *t*-BOC deprotected NC was measured using a field effect transistor (FET) made from PbSe nanocrystals. The FET structure was fabricated on a glass substrate with an imidized polyimide insulator. The fabricated FET shows p-channel characteristics. A transfer curve (Figure S4, Supporting Information) was measured in saturation and the mobility in saturation mode (μ_{sat}) is 0.01732 cm^2/V•s. This value is consistent with previous results from the literature. Specifically, the measured mobility is smaller than that of the hydrazine-treated PbSe NC FET[6] but higher than the value measured in a benzenedithiol-treated PbSe NC FET.[21] The measured mobility is sufficiently high to allow devices using *t*-BOC deprotected NCs to be used in various applications in electronic devices.

In summary, we have prepared various novel photopatternable NCs with good solubility in common solvents. The *t*-BOC protected ligands surrounding the NCs were deprotected during a chemical amplification process in the solid-state film. This change makes it possible to photopattern the NCs films. Moreover, the polarity change of the ligands provides the developer solvent-induced dual-tone (positive/negative) imaging. The shortened ligands offer improved conductivity for NC devices. The simple and straightforward ligand replacement strategy demonstrated here should be useful in the fabrication of QD-based optoelectronic devices and it should be extendible to many other NCs.

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Supporting Information Available: Experimental details and spectroscopic data.This material is available free of charge via the Internet at http://pubs.acs.org.

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